



# Electrochemical-catalytic conversion for simultaneous NO<sub>x</sub> and hydrocarbons emissions control of lean-burn gasoline engine

Ta-Jen Huang\*, Chung-Ying Wu, Sheng-Hsiang Hsu, Chi-Chang Wu

Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan, ROC

## ARTICLE INFO

### Article history:

Received 4 July 2011

Received in revised form 8 August 2011

Accepted 30 August 2011

Available online 6 September 2011

### Keywords:

Nitrogen oxide

Hydrocarbon

Lean-burn gasoline engine

Emissions control

Electrochemical-catalytic cell

Direct NO decomposition

## ABSTRACT

Electrochemical-catalytic conversion via the electrochemical-catalytic cell (ECC) is effective at 400 °C for simultaneous NO<sub>x</sub> and hydrocarbons emissions control of lean-burn gasoline engine without consuming any reductant. The NO reaction is direct NO decomposition. The NO<sub>x</sub> to N<sub>2</sub> rate over the cathode of the ECC can be three orders larger than those over conventional oxide catalysts for NO decomposition. In the high NO<sub>x</sub> concentration region, the NO conversion increases with increasing NO<sub>x</sub> concentration; this characteristic allows the engine to be operated at high enough temperature with excess oxygen to result in maximum fuel efficiency. In the low NO<sub>x</sub> concentration region, the NO conversion also increases with decreasing NO<sub>x</sub> concentration; this characteristic enables complete conversion of NO and thus can result in zero NO<sub>x</sub> emission. The NO conversion increases with decreasing temperature, at least till 400 °C. Higher oxygen concentration is beneficial to both the NO conversion and the hydrocarbons oxidation to result in zero pollution.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

The reduction of the greenhouse gases relies on increasing the energy efficiency, at least in the near future. The increase of the energy efficiency can be easily done by converting the automotive gasoline engines to lean burn so as to offer superior fuel efficiency, noting that the automobiles with gasoline engines consume a very large portion of world-wide fuel supply. However, the fuel efficiency of gasoline engines has been constrained by stoichiometric combustion for using the three-way catalytic converter so as to be able to follow the environment regulation [1]. This is a dilemma between global and local environmental protections and so far cannot be resolved due to the fact that the three-way catalytic converter cannot be used to treat lean-burn engine exhaust and other emission control technologies have difficulties to treat the exhaust with excess oxygen and high concentration NO<sub>x</sub> (NO + NO<sub>2</sub>). Note that highly efficient lean-burn engine is associated with internal combustion at high temperature with excess oxygen and thus is accompanied by high NO<sub>x</sub> concentration in the exhaust, especially of the spark-ignited gasoline engines [1]. Therefore, a technology capable of controlling high concentration NO<sub>x</sub> emission with excess oxygen is required for the realization of the lean-burn gasoline engines.

The NO<sub>x</sub> concentration in the exhaust of gasoline engine with spark ignition can be as high as 4000 ppm [1]. However, the exhaust of the lean-burn gasoline engine contains excess oxygen and thus the three-way catalytic converter, which is designed for the stoichiometric-burn engine, cannot function to reduce NO<sub>x</sub>. Currently, urea-based ammonia selective catalytic reduction (SCR) is one of the most promising technologies for NO<sub>x</sub> removal from the exhaust of the lean-burn diesel engine [2,3]. Nevertheless, the urea-SCR aftertreatment system is quite complex and has concerns including urea distribution infrastructure and potential freezing of the urea solution, other than ammonia slip as well as the inconvenience and the cost of refilling urea. Thus, every mean to achieve as low as possible NO<sub>x</sub> concentration has been used, including the extensive usage of exhaust gas recirculation [4]. This decreases the fuel efficiency of the lean-burn engines.

For NO<sub>x</sub> removal via electrochemical means, electrochemical NO reduction without using any reducing agent has been studied extensively [5]. However, this process of electrochemical NO reduction is performed with an applied current; the current efficiency is generally only a few percent since simultaneous O<sub>2</sub> reduction consumes substantial amount of electrical current [5]. Thus, electrochemical NO reduction with an applied current is not efficient for treating the engine exhaust with excess oxygen. On the other hand, simultaneous NO<sub>x</sub> reduction and power generation has been shown to be feasible via the solid oxide fuel cells (SOFCs) [6–14]; this is a SOFC-DeNO<sub>x</sub> technology. Nevertheless, although the SOFCs can generate an electricity during NO<sub>x</sub> reduction, the operation at the temperature of the engine exhaust, about 400 °C or lower, would

\* Corresponding author. Tel.: +886 3 5716260; fax: +886 3 5715408.  
E-mail address: [tjhuang@che.nthu.edu.tw](mailto:tjhuang@che.nthu.edu.tw) (T.-J. Huang).

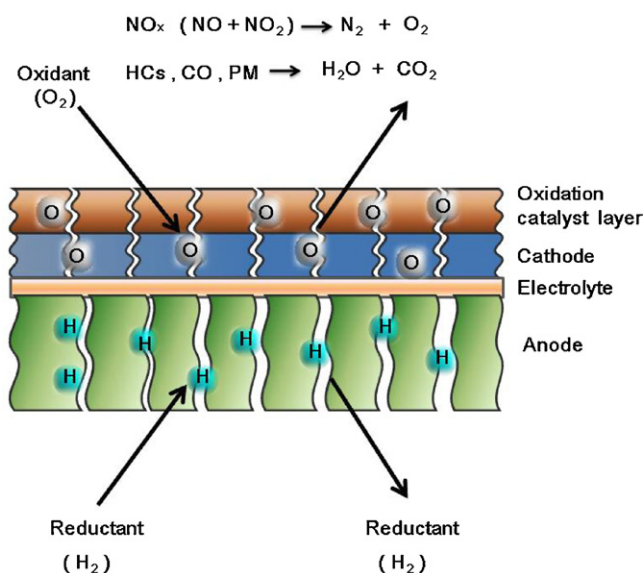


Fig. 1. Schematic of the electrochemical-catalytic cell.

generate very small amount of electricity and is thus not efficient for power generation. Therefore, a new-generation electrochemical mean has been proposed as a stack of electrochemical-catalytic cells (ECCs) [15]. An ECC is shown in Fig. 1. The ECC is simpler than conventional electrochemical cells, such as the SOFCs, by avoiding the current collecting parts. The major function of the ECC is to treat high concentration of  $\text{NO}_x$  in an engine exhaust with excess oxygen. In addition, hydrocarbons (HCs) are usually formed in the automotive gasoline engines due to cylinder wall quenching and other effects [3], and have to be treated in the exhaust aftertreatment system. On the other hand, CO and particulate matter (PM) in the exhaust of lean-burn gasoline engine should be negligible. Therefore, complete emissions control of lean-burn gasoline engine can be achieved with simultaneous  $\text{NO}_x$  and HCs treatments.

In this work, the novel technology of electrochemical-catalytic conversion is analyzed for the first time. This novel conversion is for complete emissions control to achieve zero pollution for any combustion source and is realized by the novel ECC, noting that the ECC does not consume any reductant [15] and thus can be care free. Results show that electrochemical-catalytic conversion via the ECC is especially effective for complete emissions control of lean-burn gasoline engine.

## 2. Experimental

### 2.1. Preparation of the cathode composite materials

$\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.95}\text{Cu}_{0.05}\text{O}_3$  (LSMC) was prepared by the glycine-nitrate process. Appropriate amounts of reagent-grade metal nitrates  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Showa, Japan) and  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Merck, Germany) were dissolved in de-ionized water. Glycine (Sigma, USA) was also dissolved in de-ionized water. Then, these two solutions were mixed with glycine to  $\text{NO}_3^-$  ratio of 1:1. The mixture was heated under stirring at  $110^\circ\text{C}$  until combustion occurred. The product was ground to powder and then calcined by heating to  $500^\circ\text{C}$  and held for 2 h, then to  $900^\circ\text{C}$ , held for 4 h, and then slowly cooled down to room temperature. The heat treatment of the powder was done in air with a heating rate of  $5^\circ\text{C min}^{-1}$ .  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3$  (LSMC<sub>1</sub>) and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.95}\text{Cu}_{0.05}\text{O}_3$  (LSCC) were prepared in the same way.

Gadolinia-doped ceria (GDC), with a composition of  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ , was prepared by the co-precipitation method from

reagent-grade (99.999% purity, Strem Chemical) metal nitrates  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . Appropriate amounts of gadolinium nitrate and cerium nitrate, corresponding to an atomic molar ratio of Gd:Ce = 1:9, were dissolved in de-ionized water to make 0.08 M solutions. Hydrolysis of the metal salts to hydroxides was obtained by slowly dropping each such solution into  $\text{NH}_4\text{OH}$  solution and in the meantime stirring to keep the pH of the solution  $>9$ . A distinct deep purple color of precipitate/gel was formed when the nitrate solution was dropped into  $\text{NH}_4\text{OH}$ . Vacuum filtration was employed to isolate the gel, which was then washed twice by water and ethanol. After washing, the gel was dried under vacuum at  $110^\circ\text{C}$  for 4 h, and then heated at a rate of  $10^\circ\text{C min}^{-1}$  in air to  $900^\circ\text{C}$  and held for 4 h, and then slowly cooled down to room temperature.

The LSMC–GDC composite was prepared by mixing the above-prepared LSMC and GDC powders at LSMC:GDC = 1:1 in weight. The mixture was ground for 24 h, then calcined by heating to  $500^\circ\text{C}$  and held for 2 h, and then to  $800^\circ\text{C}$ , held for 4 h. This composite was used as the cathode material. The LSMC<sub>1</sub>–GDC composite and the LSCC–GDC composite were prepared in the same way.

### 2.2. Preparation of Pd–GDC powder

The Pd–GDC powder was prepared by impregnation.  $\text{Pd}(\text{NO}_3)_2$  was dissolved in de-ionized water and then the above-prepared GDC powder was added into the solution with mixing. The impregnated powder was heated in air with a heating rate of  $5^\circ\text{C min}^{-1}$  to  $600^\circ\text{C}$  and held for 4 h. The Pd content was 1 wt% in terms of the weight of GDC.

### 2.3. Construction of the electrochemical-catalytic cell and the converter

The LSMC cell had a structure of Ni–YSZ/YSZ/LSMC–GDC/Pd–GDC. A disk of anode-supported bilayers of yttria-stabilized zirconia (YSZ) and Ni–YSZ (NexTech, Lewis Center, OH, USA) was used to make an anode-supported cell. Notably, in this bilayers disk, the average thickness of the anode layer is  $240\text{ }\mu\text{m}$  and that of the electrolyte layer is  $8\text{ }\mu\text{m}$ ; YSZ contains 8 mol% yttria. The cathode side of the bilayers was spin-coated with a thin cathode interlayer of LSMC–GDC to enhance adhesion; the coated cell was dried at  $50^\circ\text{C}$  for 6 h, then heated in air at  $10^\circ\text{C min}^{-1}$  to  $500^\circ\text{C}$  and held for 2 h, and then heated at  $5^\circ\text{C min}^{-1}$  to  $1200^\circ\text{C}$  and held for 2 h before cooling down. Then, the cell was spin-coated with LSMC–GDC as the cathode functional layer; the thus-coated cell was dried at  $50^\circ\text{C}$  for 6 h, then heated at  $10^\circ\text{C min}^{-1}$  to  $500^\circ\text{C}$  and held for 2 h, and then heated at  $5^\circ\text{C min}^{-1}$  to  $900^\circ\text{C}$  and held for 2 h. And then, the cell was spin-coated with Pd–GDC as the oxidation catalyst layer; the thus-coated cell was dried at  $50^\circ\text{C}$  for 6 h, then heated at  $10^\circ\text{C min}^{-1}$  to  $600^\circ\text{C}$  and held for 2 h. The thickness of overall cathode-side layers, i.e., cathode layers plus oxidation catalyst layer, was  $30\text{ }\mu\text{m}$  and that of overall electrochemical-catalytic cell was  $280\text{ }\mu\text{m}$ ; the total weight of overall cathode-side layers was  $5.2 \times 10^{-3}\text{ g cm}^{-2}$ . The thus-prepared cell was sealed in an electrochemical reactor to be used as an electrochemical-catalytic converter composed of a single cell, i.e., a single-cell converter. Notably, the “single-cell converter” is similar to a micro catalytic reactor; this term is based on the fact that current commercial SOFC is a stack of cells, i.e., a multiple-cell converter, to convert the anode fuel to electricity. Notably, also, the ECC is used to convert the pollutants in the exhaust to non-polluting species.

The cells with the LSMC<sub>1</sub>–GDC composite and the LSCC–GDC composite for the cathode functional layers, respectively, were prepared in the same way and termed the LSMC<sub>1</sub> cell and the LSCC cell. The material for the cathode interlayer was the same as that

for the cathode functional layer. The LSMC<sub>1</sub> cell had a structure of Ni-YSZ/YSZ/LSMC<sub>1</sub>-GDC/Pd-GDC; on the other hand, the LSCC cell had a structure of Ni-YSZ/YSZ/LSCC-GDC, *i.e.*, without coating the oxidation catalyst layer. However, the thickness of the cathode layer of the LSCC cell was about the same as that of overall cathode-side layers of the other two cells.

#### 2.4. Activity test

The NO<sub>x</sub> and HCs activity measurements were performed at 400 °C, except noted otherwise. The anode gas was pure hydrogen. The simulated lean-burn exhausts containing 10% H<sub>2</sub>O and 10% CO<sub>2</sub> always, 14% O<sub>2</sub> except noted otherwise, balance helium, with the compositions of other components of NO<sub>x</sub>, propylene (C<sub>3</sub>H<sub>6</sub>), propane (C<sub>3</sub>H<sub>8</sub>) and SO<sub>2</sub> noted in the figures and the figure legends. The flow rates on anode and cathode side were the same at 150 ml min<sup>-1</sup>. The tests were conducted with introducing the simulated exhaust to the cell cathode of the single-cell converter; a stable state was obtained for each data point. The two-cells-in-series test was done by connecting two single-cell converters in series.

The outlet gas compositions were measured throughout the test. On the cathode outlet, the NO and NO<sub>2</sub> contents were measured by NO and NO<sub>2</sub> analyzers (NGA 2000, Emerson, Germany), respectively. The N<sub>2</sub> and N<sub>2</sub>O contents were measured by gas chromatographs (China Chromatography 8900, Taiwan) equipped with thermal conductivity detector (TCD). N<sub>2</sub>O was not detected during the tests of this work. The C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> contents were measured by a gas chromatograph equipped with flame ionization detector. On the anode outlet, the H<sub>2</sub> content was measured by a TCD (China Chromatography 8900, Taiwan). For the two-cells-in-series tests, only the outlet cathode gas from the second single-cell converter was measured.

### 3. Results and discussion

#### 3.1. Electrochemical-catalytic conversion

Fig. 2 shows the scanning electron microscope (SEM) diagrams of the cross-section and the gas-side view of the cathode side of an ECC with Pd-GDC oxidation catalyst layer after the activity tests. The gas-side SEM diagram shows the porous structure; this allows the gaseous pollutants to be transported into both the oxidation catalyst layer and the cathode layers, both being also porous. It also shows the segregation of Pd, as confirmed by the energy dispersive X-ray (EDX) analysis. However, the results of EDX analysis also show that very small particles of Pd are distributed among GDC, indicating the existence of a close contact between Pd and GDC, *i.e.*, the existence of Pd-GDC. Electrochemical-catalytic conversion of NO<sub>x</sub> is considered to occur mainly in the cathode layers, consisting of the cathode interlayer and the cathode functional layer. HCs oxidation is considered to occur in both the oxidation catalyst layer and the cathode layers; however, the hard-to-oxidize species, such as propane, is considered to be mainly oxidized in the oxidation catalyst layer, such as composed of Pd-GDC. These considerations will be discussed in the following.

When operating at high enough temperature with excess oxygen, the lean-burn engines can become very fuel efficient but the NO<sub>x</sub> concentration in the engine exhaust becomes very large. This very large NO<sub>x</sub> concentration is actually welcomed by the ECC, as shown in Fig. 3 that is, in the high NO<sub>x</sub> concentration range, NO conversion increases with increasing NO<sub>x</sub> concentration; this is associated with an increase of the NO<sub>x</sub> to N<sub>2</sub> rate with increasing NO<sub>x</sub> concentration. Notably, in this work, the NO conversion is defined as (inlet NO<sub>x</sub>–outlet NO<sub>x</sub>)/(inlet NO<sub>x</sub>). Also note that the NO conversion has contributions from both NO and NO<sub>2</sub> reactions. NO<sub>2</sub>

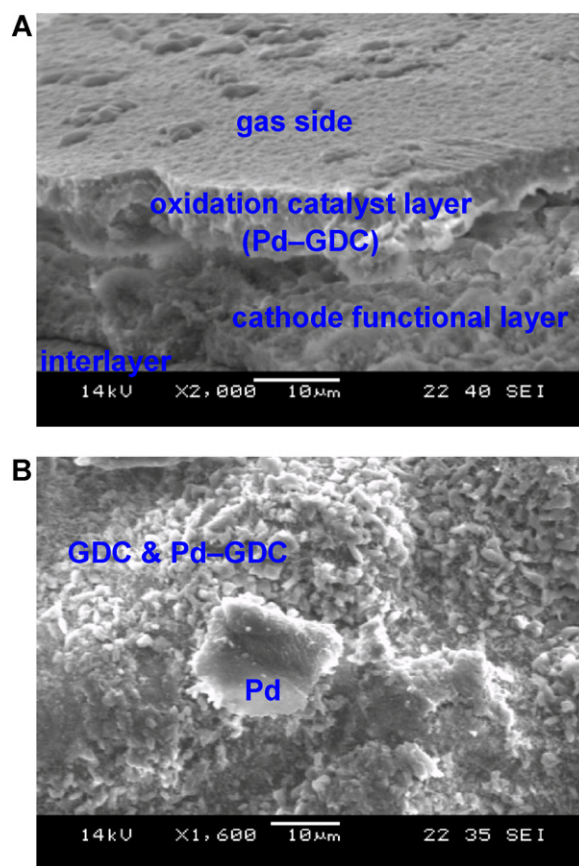


Fig. 2. SEM diagrams of (A) the cross-section and (B) the gas-side view of the cathode side of the LSMC<sub>1</sub> cell after the activity tests.

decomposes to form NO so as to decrease the NO conversion. On the other hand, NO can be oxidized to form NO<sub>2</sub> so as to increase the NO conversion; however, this does not contribute to the NO<sub>x</sub> to N<sub>2</sub> rate. Since there is no HC or other reductant in the case of Fig. 3, NO reaction should be direct NO decomposition to form N<sub>2</sub> and O<sub>2</sub>:



The occurrence of NO decomposition and the formation of N<sub>2</sub> and O<sub>2</sub> have been observed in a preliminary test under the condition without oxygen but with 9000 ppm NO at 800 °C; in this test, both the generated N<sub>2</sub> and O<sub>2</sub> can be in molar balance with the decomposed NO. However, since the oxygen concentration is very

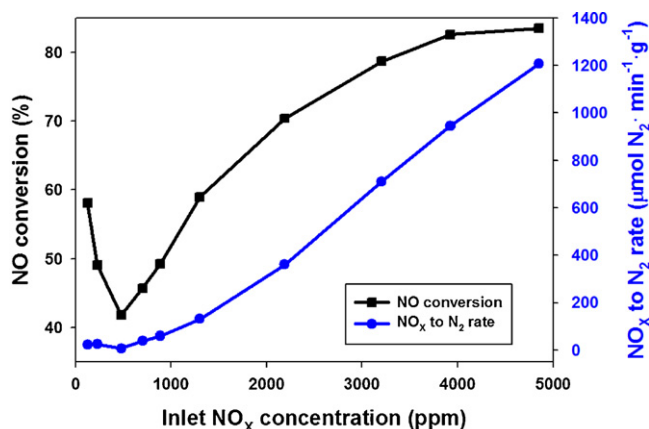


Fig. 3. Effect of NO<sub>x</sub> concentration on NO conversion and NO<sub>x</sub> to N<sub>2</sub> rate. LSMC cell at 450 °C and 100 ml min<sup>-1</sup>.

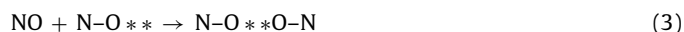


large in this work, the amount of oxygen produced via decomposition of relatively small amount of NO cannot be measured with an acceptable accuracy. It is noted that the  $\text{NO}_x$  to  $\text{N}_2$  rate over the cathode of the ECC can be three orders larger than those over conventional oxide catalysts for NO decomposition, e.g., around  $1 \mu\text{mol N}_2 \text{ min}^{-1} \text{ g}^{-1}$  at  $500^\circ\text{C}$  with 4% NO [16]. This is attributed to the well-known effect of electrochemical promotion of catalysis (EPOC) [17]. In conventional electrochemical reactors, the EPOC effect occurs due to an applied voltage [18], which generates an electromotive force (EMF).

In the ECC, the EMF is self generated by the difference between the oxygen partial pressures over the cathode and the anode [19]. Notably, although an inert gas can be used to make a difference in the oxygen partial pressures between the anode and the cathode, a reducing agent (reductant) is desirable over the anode of the ECC for a largest EMF. Hydrogen is a very good reductant; however, hydrogen is not consumed for EMF generation [15]. Thus, the reductant is used only to generate the EMF but without consumption. This is because the ECC operation is the same as the SOFC operation at open circuit; thus, there is no generation of the electricity and thus no transport of the oxygen ion from the cathode to the anode; consequently, the reductant over the anode is not consumed. Notably, also, the EMF cannot be measured in the ECC since there is no electronic connection, e.g., a metallic wire, between the cathode and the anode of the ECC. There is no electrochemical reaction occurring in the cell. Only electrochemical-catalytic conversion occurs over the cathode surface of the cell, being the same as the catalytic reaction but with electrochemical promotion.

The catalytic conversion in the ECC is promoted by an electrochemical force, i.e., the EMF, and is termed “electrochemical-catalytic conversion” in this work. In this conversion, NO is reduced via direct NO decomposition with highly promoted rate and HCs are oxidized simultaneously due to the existence of excess oxygen. Restated, NO reduction and HCs oxidation occur simultaneously over the cathode of the ECC. This conversion can offer complete emissions control, i.e., zero pollution, for lean-burn gasoline engines. Since the oxidation catalyst layer has negligible electronic conductivity at  $400^\circ\text{C}$ , the EMF should occur between the cathode layer and the anode layer. Thus, the EPOC effect should occur mainly in the cathode layer to promote the  $\text{NO}_x$  reaction. Restated, electrochemical-catalytic conversion of  $\text{NO}_x$  should occur mainly in the cathode layer. The reason for the rate promotion is further clarified in the following.

It is generally accepted [20] that the decomposition of NO involves the dissociation of NO to N and O on a catalytic surface and that N readily desorbs as  $\text{N}_2$  while O is strongly held on the surface. Catalysts active for NO decomposition should accordingly have not only the ability to adsorb and to dissociate NO but also to enable the facile desorption of oxygen. The reaction mechanism of direct NO decomposition over Co- and Mn-based perovskites has been proposed [20]:



where  $**$  is the active site as a pair of adjacent oxygen vacancies and  $\text{O}^*$  denotes O in the oxygen vacancy. In this mechanism, the formation of  $\text{N-O} **\text{O-N}$  has been proposed as the rate determining step [21,22]. However, since O is strongly held, reaction (5) for the release of oxygen has also been proposed as the rate determining step [23].

The reaction mechanism for direct NO decomposition is considered to be the same with or without electrochemical promotion.

Thus, the rate determining step in the reaction process of electrochemical-catalytic conversion is chosen as one of the above-described two proposals. Results of this work show that the formation of  $\text{N-O} **\text{O-N}$  should be the rate determining step in electrochemical-catalytic conversion; this will be clarified in the following. This is because the EPOC effect works on the release of oxygen to dramatically enhance its rate and thus reaction (5) is no longer rate determining; this makes the formation of  $\text{N-O} **\text{O-N}$  being the rate determining step. Restated, the EPOC effect enables the facile desorption of oxygen and thus accelerates the empty of the active site for successive formation of  $\text{N-O} **\text{O-N}$ ; this enhance the overall rate of direct NO decomposition. Therefore, electrochemical-catalytic conversion means electrochemically promoted catalytic conversion. For the ECC, electrochemical-catalytic conversion means direct NO decomposition promoted by the self-generated EMF.

It is generally agreed [24] that the formation of  $\text{N}_2$  is directly caused from the collision of two activated nitrogen atoms and the formation of  $\text{O}_2$  occurs via the combination of the two left oxygen atoms, in agreement with the reaction mechanism of steps (2)–(5). It is also proposed [20] that the release of oxygen, reaction step (5), is regulated by the adsorption–desorption equilibrium of oxygen. Over the cathode of the ECC,  $\text{O}_2$  dissociation should occur:



where  $**$  is the same active site for NO adsorption and decomposition, i.e., a pair of adjacent oxygen vacancies. Then, adsorption–desorption equilibrium of oxygen over the cathode of the ECC can be accomplished in the same way as that of the SOFC. Thus, the reverse of reaction (6), i.e., reaction (5), can be very fast. This is attributed to the self-generated voltage, i.e., the self-generated EMF. In other word, reaction (5) can be very fast in the ECC. Notably, the O species is considered to be taken into the oxygen vacancy of the ECC cathode in the same way as that of the SOFC cathode. Since the occurrence of reaction (5) should not discriminate the source of the O species, reaction (5) during NO decomposition can be as fast as that during adsorption–desorption equilibrium of gaseous oxygen.

### 3.2. Effect of $\text{NO}_x$ concentration

Fig. 3 also shows that there is a minimum in the NO conversion as the  $\text{NO}_x$  concentration varies from the low  $\text{NO}_x$  concentration region to the high  $\text{NO}_x$  concentration region. Low  $\text{NO}_x$  concentration side of the minimum, i.e., in the low  $\text{NO}_x$  concentration region, shows a characteristic of increasing NO conversion with decreasing  $\text{NO}_x$  concentration. This characteristic enables complete conversion of NO and thus can result in zero emission of NO. This characteristic has been reported for electrochemical  $\text{NO}_x$  reduction at  $800^\circ\text{C}$  without the presence of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ; complete conversions of both NO and  $\text{NO}_2$  have been observed [7]. Note that  $\text{NO}_2$  dissociates to form NO:



with the produced O species taken into an oxygen vacancy. Thus, complete conversion of NO can result in complete conversion of  $\text{NO}_2$ . This characteristic has also been observed for catalytic NO decomposition at  $400^\circ\text{C}$ , also without the presence of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  [25].

High  $\text{NO}_x$  concentration side of the minimum, i.e., in the high  $\text{NO}_x$  concentration region, shows a characteristic of increasing NO conversion with increasing  $\text{NO}_x$  concentration. Thus,  $\text{NO}_x$  of very high concentration can be reduced easily, the higher the  $\text{NO}_x$  concentration the better. This characteristic allows the engine to be operated at high enough temperature with excess oxygen to result in maximum fuel efficiency, which is associated with very high

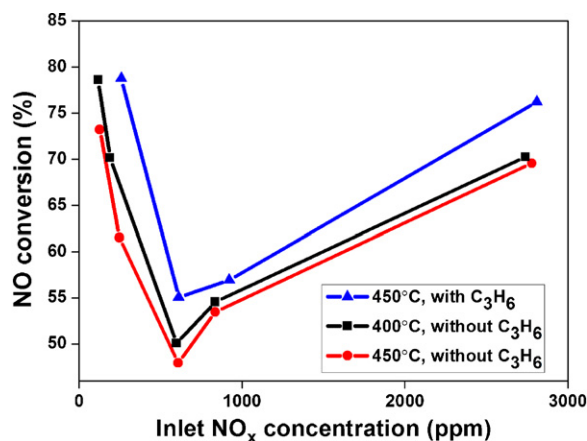


Fig. 4. Effect of  $\text{NO}_x$  concentration, temperature and propylene on NO conversion. LSCC cell at 400 and 450 °C with or without 350 ppm  $\text{C}_3\text{H}_6$ ; other component was 25 ppm  $\text{SO}_2$ .

$\text{NO}_x$  concentration. This characteristic of increasing NO conversion with increasing  $\text{NO}_x$  concentration in the high  $\text{NO}_x$  concentration region is associated with increasing  $\text{NO}_x$  to  $\text{N}_2$  rate, as also shown in Fig. 3. However, the increase of the conversion becomes flattened at the  $\text{NO}_x$  concentration becomes larger than about 4000 ppm. Note that the highest  $\text{NO}_x$  concentration in the exhaust of automotive gasoline engine with spark ignition is about 4000 ppm [1]; thus, this flattened conversion will not affect the ECC performance of  $\text{NO}_x$  emission control for gasoline engines. Notably, the conversion curve should become flattened when the conversion approaches 100%.

In the high  $\text{NO}_x$  concentration region, the increase of the rate with the  $\text{NO}_x$  concentration shows an effect of the reaction kinetics – that is, the rate increases with increasing concentration. This indicates that the rate is determined by the  $\text{NO}_x$  concentration. Since this result is not associated with the release of oxygen, the formation of  $\text{N-O}^*\text{O-N}$  should be the choice as the rate determining step. Then, high concentration of  $\text{N-O}^*\text{O-N}$  results in high rates of reactions (4) and (5) successively. Additionally, since the  $\text{NO}_x$  to  $\text{N}_2$  rate with either very high or very low concentration of  $\text{NO}_x$  does not seem to be inhibited by the very large amount of oxygen, NO adsorption should be stronger than  $\text{O}_2$  adsorption, at least over the cathode materials of this work.

In the low  $\text{NO}_x$  concentration region, the characteristic of increasing NO conversion with decreasing  $\text{NO}_x$  concentration is due to an almost constant  $\text{NO}_x$  to  $\text{N}_2$  rate, as also shown in Fig. 3. Notably, the increased NO conversion with decreasing  $\text{NO}_x$  concentration is a calculated result according to the definition of the NO conversion. This independence of the rate on the  $\text{NO}_x$  concentration indicates that other factor instead of the reaction kinetics is working here. This factor is very possibly the surface diffusion of the adsorbed NO species. It is noted that, since NO adsorption is stronger than  $\text{O}_2$  adsorption, NO can be almost completely adsorbed but  $\text{N-O}^*\text{O-N}$  is not formed due to scattered NO adsorption over the surface under low  $\text{NO}_x$  concentration. For the formation of  $\text{N-O}^*\text{O-N}$ , NO must diffuse across the surface to get together. This again indicates that the formation of  $\text{N-O}^*\text{O-N}$  is the rate determining step. However, in this case, the formation of  $\text{N-O}^*\text{O-N}$  is by NO diffusion to  $\text{N-O}^*$  via the surface instead of adsorption from the gas phase, the latter being reaction (3).

### 3.3. Effect of adding propylene

Fig. 4 shows that both decreasing temperature and adding propylene increase the NO conversion; in addition, the effect of adding 350 ppm propylene is larger than that of decreasing

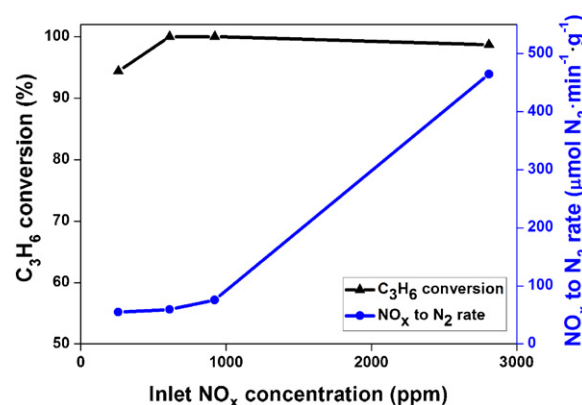


Fig. 5. Effect of  $\text{NO}_x$  concentration on propylene conversion and  $\text{NO}_x$  to  $\text{N}_2$  rate. LSCC cell at 450 °C with 350 ppm  $\text{C}_3\text{H}_6$ ; other component was 25 ppm  $\text{SO}_2$ .

temperature from 450 to 400 °C. The effect of temperature will be discussed in Section 3.5. The effect of adding propylene is due to the reaction between propylene and  $\text{NO}_x$ , similar to that for HC-De $\text{NO}_x$  over catalyst [26]. Notably, propylene is usually used to represent HC in the engine exhaust [27].

Fig. 5 shows that the propylene conversion can become 100%. However, the propylene conversion decreases slightly when the  $\text{NO}_x$  concentration increases towards very high concentration. This indicates an inhibition of propylene conversion by  $\text{NO}_x$  and can be attributed to stronger adsorption of  $\text{NO}_x$  than propylene. On the other hand, the propylene conversion also decreases when the  $\text{NO}_x$  concentration decreases towards very low concentration. This is attributed to not enough activity of HC-De $\text{NO}_x$  to enhance propylene conversion. However, the decreased extent of propylene conversion is small. This indicates that the major reaction for propylene conversion should be its oxidation by the O species from gaseous oxygen, which is in large excess. Note that there should be no discrimination between the sources of the O species for propylene oxidation. On the other hand, in the low  $\text{NO}_x$  concentration region, the  $\text{NO}_x$  to  $\text{N}_2$  rate is also constant in the presence of propylene; HC-De $\text{NO}_x$  may have some contribution for this constant rate. However, this needs further studies for clarification.

### 3.4. Effect of $\text{O}_2$ concentration

Fig. 6 shows that the HCs conversions increase dramatically when the oxygen concentration increases to about 6%. Notably,

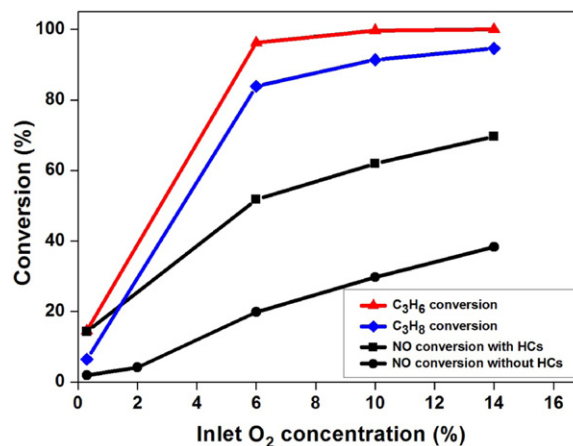


Fig. 6. Effect of  $\text{O}_2$  concentration. LSMC<sub>1</sub> cell at 450 °C with two-cells-in-series tests; other components were 2536 ppm  $\text{NO}_x$ , 0.3–14%  $\text{O}_2$  and 25 ppm  $\text{SO}_2$ , with or without HCs (propylene and propane: 318 ppm  $\text{C}_3\text{H}_6$  and 93 ppm  $\text{C}_3\text{H}_8$ ).

propylene and propane are usually used to represent HCs in the engine exhaust [27]. It is noted that the propylene conversion can become 100% either in the ECC with an oxidation catalyst layer, as shown in Fig. 6, or in the ECC without it, as shown in Fig. 5. This confirms the above consideration that HCs oxidation occurs in both the oxidation catalyst layer and the cathode layers. However, the existence of the oxidation catalyst layer can help the oxidation of the hard-to-oxidize species; preliminary test shows that propane conversion is relatively small in the absence of the oxidation catalyst layer and may result in the deactivation of the cathode layers.

When an oxidation catalyst layer made of Pd–GDC is added in the ECC, propane could be oxidized easily in a similar way as that over Pd/La<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3</sub> catalyst at 400 °C [27]. Note that both GDC and La<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3</sub> contain the oxygen vacancies. When the oxygen vacancies exist in the neighborhood of Pd, propane can be adsorbed onto Pd and then oxidized by the O species formed in reaction (6) from O<sub>2</sub> dissociation. Note that propane oxidation can form either CO or CO<sub>2</sub> [28]. Thus, the reactions of the C species of propane with the O species are considered as:



The occurrence of these reactions depends on a close contact between Pd and GDC, *i.e.*, the existence of Pd–GDC, which has been confirmed by the EDX analysis in association with the SEM analysis of Fig. 2B.

Fig. 6 also shows that the conversion of propane is smaller than that of propylene; this is similar to that over Pd/La<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3</sub> catalyst also at 400 °C [27]. When the oxygen concentration is small, both the HCs and the NO conversions are small. The results in Fig. 6 indicate that the major reaction for HCs conversions should not be HC–DeNO<sub>x</sub> but is the oxidation by the O species from gaseous oxygen, in accordance with the above observation. However, HC–DeNO<sub>x</sub> does contribute to the NO conversion, as indicated by the difference between the NO conversions with and without the presence of HCs; this is also in accordance with the above observation. In addition, the extent of the HC–DeNO<sub>x</sub> contribution increases as the oxygen concentration increases to about 6%, when the NO conversion increases considerably with increasing oxygen concentration in the presence of HCs.

Fig. 6 also shows that the NO conversion increases with increasing oxygen concentration with or without the presence of HCs. This is attributed to the fact that higher oxygen concentration over the cathode can result in larger EMF, which is equivalent to the open-circuit voltage in the SOFCs [29]. Notably, no matter how much the oxygen content is in the engine exhaust, secondary air can be added into the exhaust pipe to increase the oxygen concentration in the exhaust so as to increase both the NO conversion and the HCs oxidation.

### 3.5. Effect of temperature

Fig. 7 shows that both the NO conversion and the NO<sub>x</sub> to N<sub>2</sub> rate decrease with increasing temperature. Notably, the effective operating temperature of 400 °C for the ECC is near the temperature of the exhaust from the engine during its normal operation. However, when the engine misfires, a large quantity of unburned fuel is sent through the exhaust pipe; this can cause considerable temperature increase in the same way as in the three-way catalytic converter [30]. Long acceleration can also cause an increase of the cell temperature. Nevertheless, a comparison of Figs. 6 and 7 shows that the extent of variation of the NO conversion with the temperature is much smaller than that with the oxygen concentration. This is beneficial for the operation of the ECC onboard automobiles.

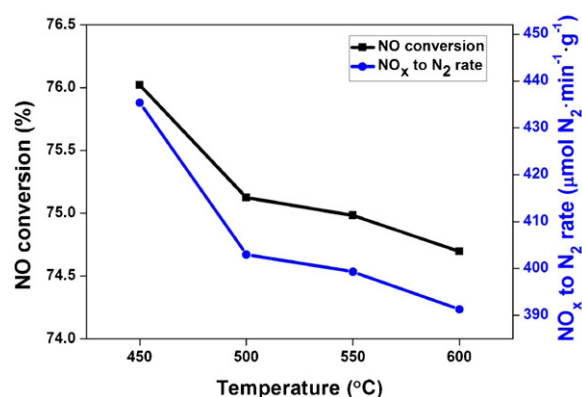


Fig. 7. Effect of temperature. LSCC cell, 2814 ppm NO<sub>x</sub> and 25 ppm SO<sub>2</sub>.

The decrease of the DeNO<sub>x</sub> rate with increasing temperature is attributed to two factors. One is that NO decomposition is exothermic; thus, higher temperature is detrimental to its thermodynamic equilibrium. However, this effect becomes significant only when the conversion is near the equilibrium one. The other is that, when the cell temperature increases, the open-circuit voltage decreases [11]; thus, the EPOC effect decreases to result in smaller NO conversion. On the other hand, the increase of the DeNO<sub>x</sub> rate with decreasing temperature, at least till 400 °C, is beneficial for the ECC to be operated at a temperature close to those of current emissions control technologies, which is generally around or below 400 °C.

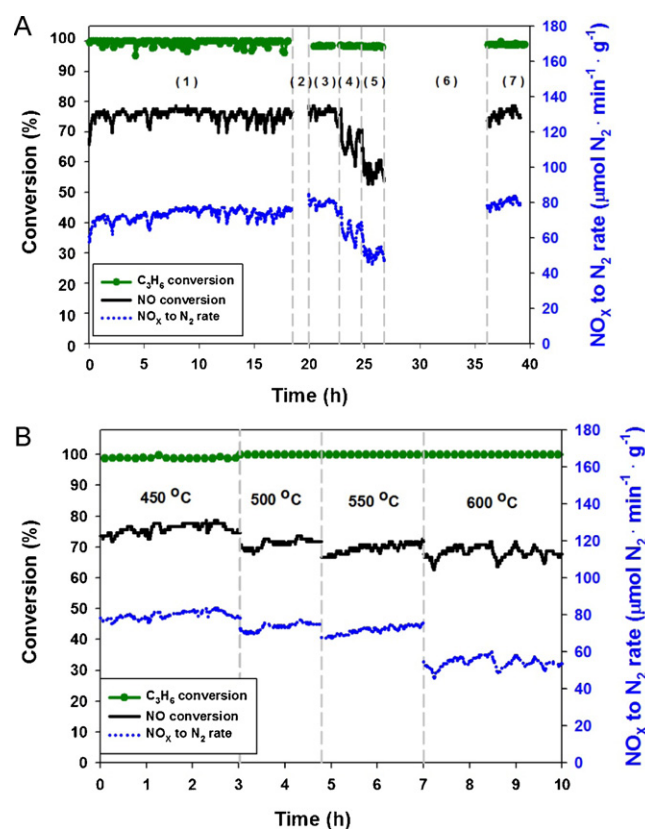


Fig. 8. Performance under simulated conditions. LSCC cell at 450 °C and 100 ml min<sup>-1</sup>. (A) Other components during (1), (3) and (7): 301 ppm NO<sub>x</sub>, 300 ppm C<sub>3</sub>H<sub>6</sub> and 26 ppm SO<sub>2</sub>; (2) and (6): 20% O<sub>2</sub> in helium; (4): same as (1) except with 10% O<sub>2</sub>; (5): same as (1) except with 6% O<sub>2</sub>. (B) Other components were the same as (1) in (A).

### 3.6. Long term performance

Fig. 8A shows that propylene can be completely converted. Since electrical conductivity is not required by the oxidation catalyst layer of the ECC, any catalyst can be considered to make this layer so as to take advantage of the well-established oxidation technologies. It is seen that the  $\text{NO}_x$  to  $\text{N}_2$  rate increases with time; this is due to the activation of the electrode materials of the ECC under long term operation, similar to that of the SOFCs [31]. It is also shown that higher oxygen concentration results in both higher NO conversion and larger  $\text{NO}_x$  to  $\text{N}_2$  rate, in accordance with the above results. In addition, after the ECC was kept in air for over 9 h, simulating the condition for a truck stop, the  $\text{DeNO}_x$  activity actually increases, although slightly. This is in agreement with the positive effect of oxygen on direct NO decomposition over the ECC.

Fig. 8B shows that, when the operating temperature of the cell increases from 450 to 600 °C, both the NO conversion and the  $\text{NO}_x$  to  $\text{N}_2$  rate decrease. This is in accordance with the above results on the temperature effect. However, a comparison of Figs. 7 and 8B shows that the extent of variation of either the NO conversion or the  $\text{NO}_x$  to  $\text{N}_2$  rate with temperature in the high  $\text{NO}_x$  concentration region is much smaller than that in the low  $\text{NO}_x$  concentration region. This dependence of the extent of variation of NO conversion with temperature on the  $\text{NO}_x$  concentration is the same as that shown in Fig. 4. This is beneficial for the ECC to treat an engine exhaust with high  $\text{NO}_x$  concentration, which is the case for highly efficient lean-burn gasoline engine. Notably, since the commercial SOFC used as the auxiliary power unit for the truck can be used for over 5 years, the ECC with simpler structure and lower operating temperature than those of the SOFC may be used longer.

## 4. Conclusions

Electrochemical-catalytic conversion via the electrochemical-catalytic cell (ECC) is effective at 400 °C for complete emissions control of lean-burn gasoline engine without consuming any reductant. The NO reaction is direct NO decomposition. The  $\text{NO}_x$  to  $\text{N}_2$  rate over the cathode of the ECC can be three orders larger than those over conventional oxide catalysts for NO decomposition due to electrochemically promoted catalytic conversion. In the high  $\text{NO}_x$  concentration region, the NO conversion increases with increasing

$\text{NO}_x$  concentration; this characteristic allows the engine to be operated at high enough temperature with excess oxygen to result in maximum fuel efficiency. In the low  $\text{NO}_x$  concentration region, the NO conversion also increases with decreasing  $\text{NO}_x$  concentration; this characteristic enables complete conversion of NO and thus can result in zero emission of NO. The NO conversion increases with decreasing temperature, at least till 400 °C. Higher oxygen concentration is beneficial to both the NO conversion and the HCs oxidation.

## References

- [1] L. Guzzella, C.H. Onder, Introduction to Modeling and Control of Internal Combustion Engine Systems, Springer-Verlag, Berlin, 2010.
- [2] A.T. Krishnan, A.L. Boehman, Appl. Catal. B 18 (1998) 189–198.
- [3] M. Koebel, M. Elsener, M. Kleemann, Catal. Today 59 (2000) 335–345.
- [4] M. Zheng, G.T. Reader, J.G. Hawley, Energy Conv. Manag. 45 (2004) 883–900.
- [5] K. Kammer, Appl. Catal. B 58 (2005) 33–39.
- [6] T.J. Huang, C.L. Chou, Electrochem. Commun. 11 (2009) 477–480.
- [7] T.J. Huang, C.L. Chou, J. Electrochem. Soc. 157 (2010) P28–P34.
- [8] T.J. Huang, C.L. Chou, Chem. Eng. J. 160 (2010) 79–84.
- [9] T.J. Huang, C.L. Chou, Chem. Eng. J. 162 (2010) 515–520.
- [10] T.J. Huang, I.C. Hsiao, Chem. Eng. J. 165 (2010) 234–239.
- [11] T.J. Huang, C.Y. Wu, C.C. Wu, Chem. Eng. J. 168 (2011) 672–677.
- [12] T.J. Huang, C.Y. Wu, C.C. Wu, Electrochem. Commun. 13 (2011) 755–758.
- [13] T.J. Huang, C.Y. Wu, Y.H. Lin, Environ. Sci. Technol. 45 (2011) 5683–5688.
- [14] T.J. Huang, C.Y. Wu, C.C. Wu, Chem. Eng. J. 172 (2011) 665–670.
- [15] T.J. Huang, C.Y. Wu, S.H. Hsu, C.C. Wu, Energy Environ. Sci. (2011), doi:10.1039/c1ee01792f.
- [16] T. Yamashita, A. Vannice, J. Catal. 163 (1996) 158–168.
- [17] S. Brosda, C.G. Vayenas, J. Wei, Appl. Catal. B 68 (2006) 109–124.
- [18] S. Bredikhin, K. Hamamoto, Y. Fujishiro, M. Awano, Ionics 15 (2009) 285–299.
- [19] L. Suski, J. Kołacz, G. Mordarski, M. Ruggiero, Electrochim. Acta 50 (2005) 2771–2780.
- [20] Y. Teraoka, T. Harada, S. Kagawa, J. Chem. Soc. Faraday Trans. 94 (1998) 1887–1891.
- [21] M. Haneda, Y. Kintaichi, H. Hamada, Appl. Catal. B 55 (2005) 169–175.
- [22] J. Zhu, D. Xiao, J. Li, X. Yang, Y. Wu, J. Mol. Catal. A 236 (2005) 182–186.
- [23] E.R.S. Winter, J. Catal. 22 (1971) 158–170.
- [24] J. Zhu, A. Thomas, Appl. Catal. B 92 (2009) 225–233.
- [25] Z. Liu, J. Hao, L. Fu, T. Zhu, Appl. Catal. B 44 (2003) 355–370.
- [26] R. Burch, J.P. Breen, F.C. Meunier, Appl. Catal. B 39 (2002) 283–303.
- [27] C.H. Kim, G. Qi, K. Dahlberg, W. Li, Science 327 (2010) 1624–1627.
- [28] W.L.S. Faria, L.C. Dieguez, M. Schmal, Appl. Catal. B 85 (2008) 77–85.
- [29] T.J. Huang, C.L. Chou, J. Power Sources 193 (2009) 580–584.
- [30] M.R. Ilkivová, B.R. Ilkiv, T. Neuschl, Control Eng. Practice 10 (2002) 1141–1146.
- [31] C.H. Wang, M.C. Lee, T.J. Huang, Y.C. Chang, W.X. Kao, T.N. Lin, Electrochem. Commun. 11 (2009) 1381–1384.